Session VII
ODS Management/Reduction

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ALTERNATIVE DEGREASING FOR COMPOSITE HONEYCOMB REPAIR

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REGULATORY BACKGROUND

Ozone-Depleting Chemicals

The Montreal Protocol was first implemented in the United States in February 1989 when the EPA issued the final rule "Protection of the Stratospheric Ozone" in the Federal Register (40 CFR Part 82). In 1990, Congress passed the Clean Air Act Amendments. Title VI of these amendments codified the Montreal Protocol production bans and identified 1,1,1 trichloroethane (methyl chloroform, TCA) as a Class I ODC. It also allowed the EPA to further restrict ODC production as the science of ozone depletion developed. In February 1992, President Bush exercised this authority by accelerating the phase-out of Class I ODCs, banning domestic production of halon after January 1, 1994 and all remaining Class I ODCs after January 1, 1996.

In October 1992, Congress enacted unique restrictions on the DoD through the Defense Authorization Act for Fiscal Year 1993 (Public Law 102-484). Section 326 of that law prohibits the DoD from letting contracts that require the use of a Class I ODC. This law predicated the establishment of a detailed contract review process, to be able to identify existing ODC call-outs. Each Service reports approved waivers, initially quarterly and now annually, to Congress.

Toxic Chemicals

In August of 1993, President Clinton signed Executive Order 12856. It's purpose is to "ensure that all federal agencies conduct their facility management and acquisition activities so that, to the maximum extent practicable, the quantity of toxic chemicals entering the wastestream, including any releases to the environment, is reduced as expeditiously as possible through source reduction." Toxic chemicals are identified as "a substance on the list described in section 313(c) of EPCRA." Trichloroethylene (TCE), CAS Number 79-01-6, is identified on this list.

TCE is also one of the 17 high-priority toxic chemicals identified by the EPA's 33/50 Program, with the goal of reducing environmental releases and off-site transfers by 33% in 1992 and 50% in 1995. The Army also identified TCE for special attention when it was reported as one of the top 17 toxic chemicals in the Army's 1995 Toxic Release Inventory (TRI) report.

HONEYCOMB CLEANING

Most work areas at the Corpus Christi Army Depot (CCAD) helicopter maintenance facility have switched from TCA to aqueous-based cleaning systems. These systems are sufficient for cleaning grease and other general contaminants from parts with readily accessible surfaces. Water based cleaning has not proven to be compatible with composite honeycomb parts, however, because they must be completely dry and residue-free before the honeycomb core and skin are adhered. Moisture introduced into the autoclave curing process will expand as it evaporates, which can cause adhesive disbonding, honeycomb damage, or even skin damage.

Portions of damaged helicopter honeycomb skin panels are removed during repair procedures. Replacement portions of aluminum or Nomex honeycomb and skin are then patched into the panels. The aluminum honeycomb is 2024 series aluminum. Composite honeycomb is made of Nomex material. The honeycomb core is typically 0.375 – 0.500 inch thick, with a cell size as small as 0.125 inch and density up to 35 cells per square inch. Floor boards and cargo doors are the must common components processed. These honeycomb panels are typically 20-25 square feet, and can be as large as 75 square feet.

Honeycomb composite repair is classified as either minor or major. A major repair is where the honeycomb core has been significantly damaged and must be replaced. A minor repair is where the damage is only to the skin, or there is a delaminated area where the skin no longer is bonded to the honeycomb core. It is very difficult to affectivity remove all of the contaminants from the tight honeycomb structure below the damage of a minor repair. It is also very difficult to dry the recessed areas of the honeycomb if the cleaning material does not quickly evaporate.

The honeycomb shop had used a small TCA vapor degreaser with a 4 foot x 4 foot x 3 foot tank. At this time, the honeycomb composite repair shop is manually hand-wiping the repair surfaces using Lectra Clean, a TCE product which comes in an aerosol can. When using TCA or TCE, the parts are dry after cleaning. There are therefore no specific process time constraints that dictate how quickly an alternative material needs to evaporate. One of the key concerns expressed by the repair personnel, however, is for the solvent to dry fast and leave no residue. Typical total-repair process time for a large floorboard may take over 70 hours, so any additional time spent waiting for the part to dry (or drying the part) is significant.

No testing is done to verify the cleanliness of the surface in the shop, other than visual inspection. If a part is found to have not been properly cleaned, it is deemed uncleanable and thrown away. CCAD periodically tests the adhesive bond strength of its repaired parts, however, and in this way infers the part's cleanliness before bonding. If a piece fails this test, then a failure analysis is conducted to determine if the failure was due to improper cleaning, bad adhesive, or defective test materials. Tests include T-peel, lap sheer, and climbing drum peel mechanical tests. In the case of vapor degreasers, the solvent reservoirs are monitored on a regular schedule to make sure that the solvent concentrations, temperatures, etc. are within the design parameters.

TECHNICAL APPROACH

The requirements for an alternative cleaning material and/or process were identified as:

a. It remove the same contaminants from the surface to the same level as TCA.
b. It dry quickly without significant residue.
c. It not create the need for a large new piece of equipment.
d. It cause minimal worker health impacts (not carcinogenic, mutagenic, etc.).
e. It has minimal environmental impacts (low VOC, non-ODC, etc.).
f. It have minimal safety impacts (low flammability, low explosion risk, etc.).

The project had two phases: 1) engineering analysis and laboratory evaluation, and 2) demonstration of recommended cleaning system(s) in the composite shop. All the laboratory tests are briefly described in this paper.

Test Materials

The following is are the alternative cleaning agents evaluated under this program.

Triagen – Ecolink, Inc.
An alkyl bromide-based (normal propyl bromide) blend available in aerosol form

Positron – Ecolink, Inc.
A terpene-based (heavy hydrocarbon), high purity dielectric solvent.

Vertrel MCA Plus – Dupont Fluoroproducts
An azeotrope of hydrofluorocarbons with trans-1,2-dichloroethylene and cyclopentane.

Oxsol 100 - Occidental Chemical Corp.
A fluorinated toluene whose chemical name is parachlorobenzotrifluoride.

OS-120 - Dow Corning Corp.
An azeotrope of volatile methyl siloxanes (VMS) developed for precision cleaning.

HFE-7100 - 3M Chemicals
A hydrofluoroether (HFE) compound, specifically methoxynonafluorobutane.

Envirosolve 655 - Fine Organics Corporation
A solvent blend of an isoparaffinic hydrocarbon and a proprietary organic solvent.

SC 431 - Calgon Corp.
A non-chlorinated solvent made from a petroleum distillate blend.

Pure ethyl lactate
An extremely fast evaporating, organic solvent currently used as a food additive.

DS 108 - Dynamold Solvents, Inc.
A precision hand wipe solvent whose principle constituent is ethyl propionate.

HyperSolve-NPB – Great Lakes Chemical Corp.
An n-propyl bromide based chemical blend designed for vapor degreasing.

Partsprep – Ecolink, Inc.
A solvent blend whose principle constituent is n-methyl pyrrolidone (NMP).

Test Methods

First, engineering research was conducted on the candidate solvents to gather technical information in the following four main areas:

1. Physical properties of the cleaner, as related to the cleaning process.
2. Ability of the alternative to clean.
3. Effect of the cleaner on the structural materials of the helicopters.
4. Environmental, worker health and safety issues related to the cleaner/process.

I. *Physical Properties of the Cleaning Material*

Physical properties such as boiling point and flash point were collected for chemicals of each material family. The evaporation rates, deemed critical to the composite shop cleaning process and not listed on all the MSDS, were verified through the following tests.

Evaporation Rate. ASTM D1901, "Relative Evaporation Time of Halogenated Organic Solvents and Their Admixtures." This test involves pouring the solvent over a panel with a scribed edge. The time is recorded when a break in the continuity of the coverage occurs. The time is also recorded when the residue can no longer be detected along the scribe. This test was repeated in triplicate and then compared to the times of the controls (TCA and TCE).

Gravimetric Testing. A known volume of solvent was placed in a pre-weighed aluminum container. The change in weight of the solution was monitored over time, as was temperature and humidity. The mass-loss rate was used to compare the rate for different cleaning materials.

II. Cleaning Ability

Tests conducted to evaluate the cleaning ability of the material were chosen for their relationship to current procedures performed at CCAD, as well as ASTM standard procedures. Cleaning efficiency was measured by taking the amount of soil removed by a cleaner based on gravimetric calculations. Visual examination and physical testing of bonded joints was also done.

Preparation. ASTM G-121, "Preparation of Contaminated Test Coupons for the Evaluation of Cleaning Agents." Test panels were cleaned with an acetone rinse to prepare uniform surfaces and pre-weighed. They were then rinsed in solutions containing different contaminants. The panels were then dried and weighed.

Cleaning Efficiency. ASTM G-122, "Standard Test Method for Evaluation the Effectiveness of Cleaning Agents." The composition of the contaminant was MIL-L-23699 (50 gm), MIL-H-5606 (50 gm), LIM-H-83282 (50 gm), 2024 aluminum shavings (5 gm), and Nomex and Kevlar "dust" (2.5 gm each). The panels were cleaned in the various test solutions, dried, and re-weighed. The weight of soil remaining on the panel was determined, and the cleaning efficiency was calculated for each test material. Visual examination was also used to identify and examine any residue that remained on the panel surface.

Adhesive Bond Strength. ASTM D1002, "Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal)." This test evaluated the quality of the cleaning process by through the adhesive strength of the subsequent bonded structure. Overlapped panels were bonded after cleaning with the alternate cleaners. The specimens were then placed in a tensile loading machine and a load was applied until failure occurred. The failure loads were recorded and compared to standard values. Bond failures were also analyzed to determine where the failures occurred - at the adhesive bond layer, within the adhesive material, or within the material.

III. Physical Effects of Cleaner on Substrates

It was also important to determine if the alternate cleaners had any affect on the basic mechanical properties of the substrate. Testing was conducted on samples of 2024 aluminum and Nomex/Kevlar composites. Information was also gathered from the failure analysis of the physical testing conducted to evaluate the cleanability of the alternate materials.

Immersion Corrosion. ASTM F483, "Total Immersion Corrosion Test for Aircraft Maintenance Chemicals." Samples of substrate materials were pre-weighed and then immersed at a constant temperature of 38 $\pm$3 °C (100 $\pm$5 °F). The solution volume-to-material area ratio was at least 8 ml/cm^2. After 24 hours of immersion, the samples were dried and weighed again with appearance noted. Then the samples were again immersed for another 144 hours. The weight and visual changes were again recorded. Finally, the weight gain or loss was calculated.

Tests were also performed to evaluate the effects of the cleaners on composites during exposure by measuring the increase in weight of the polymer test samples in relation to the time of immersion. This testing was based on ASTM D5229, "Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials."

Sandwich Corrosion. ASTM F1110, "Sandwich Corrosion Test." Each solution was added to a set of three panels. Each day the panels were placed in the humidity chamber at 95-100% humidity, and 37.7°C (100°F) for 8 hours. Panels were then oven dried at 37.7°C (100°F). After exposure, panels were rinsed and visually inspected for corrosion.

Effects on Unpainted Surfaces. ASTM F-485, "Effects of Cleaners on Unpainted Aircraft Surfaces." Two panels of each substrate were cleaned to ensure clear results. Specimens were immersed for 3-5 minutes in the cleaning solution that covered half the panel, followed by drying for 30 minutes in a convection oven at 150°F (65.5°C). After cooling, the panels were rinsed with tap water for one minute and then distilled water for 15 seconds. The panels were then visually examined by comparing the immersed and untreated parts against one another.

IV. Environmental, Worker Health, and Safety Issues

Information was gathered on environmental, health, and safety issues for each of the alternate materials in addition to test performance data.

CONCLUSIONS

The following conclusions summarize the results from the engineering analysis, phase 1, and phase 2 testing. Details on the results of the testing, as well as the raw test data, are contained in the body and appendices of "Alternative Degreasing for Composite Honeycomb Repair," prepared for the U.S. Army Industrial Operations Command, Corpus Christi Army Depot, dated 31 March 1998.

Conclusion #1: Only two of the candidate solvents satisfied all the key requirements identified: HFE-7100 and Vertrel MCA (Plus). Both cleaned as well and evaporated as fast as TCA and TCE, do not require new equipment, have minimal health impacts (200 and 600 parts per million exposure limits, respectively), are VOC exempt, and are non-flammable. Both are therefore acceptable alternatives.

Conclusion #2: Two other candidates, Triagen/Hypersolve and OS-120, were also considered acceptable alternatives. They cleaned as well and demonstrated evaporation rates on a par with TCA and TCE, do not require new equipment, and have acceptable limits of 200 parts per million. They also both cost considerably less than HFE 7100 and Vertrel MCA (Plus). OS-120, however, is a flammable liquid and requires special storage and handling considerations.

Conclusion #3: There is some concern over the performance of Vertrel MCA (Plus) in the demonstration conducted on the shop floor. Subjective comments were received that it did not adequately clean certain oil and hydraulic fluid from the honeycomb core. This should be further defined and analyzed before the HFC is implemented in the shop.

Conclusion #4: Further testing should be accomplished to identify the performance of these four solvents in other hand-wipe and vapor degreaser applications in CCAD for the potential replacement of other hazardous or toxic solvents.

Conclusion #5: Further testing should be accomplished to pursue the use of pure ethyl lactate. This material is not yet ready for use in a major industrial application, but the small sample that was acquired performed very well in the tests in which it participated. Limited available quantities currently force the price beyond all the other solvents. As more interest is generated, however, more product will be produced and the price should come down to at least that of the HFEs and HFCs.

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